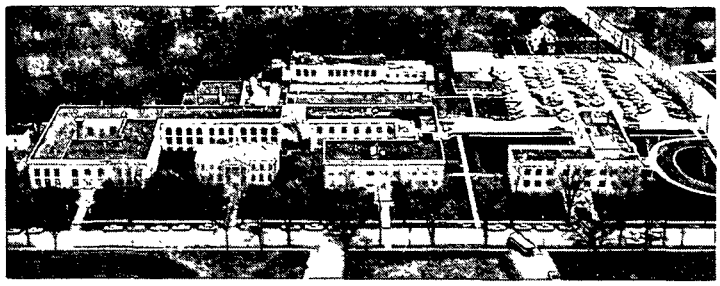

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CORROSION IN CLOSED WHITE WATER SYSTEMS

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ABSTRACT

The corrosion of metals by paper machine white water may be uniform or localized. The corrosivity of recycle white water in "closed" systems is a matter of great importance in design. A research program to evaluate both corrosion forms is described. Uniform corrosion test results for mild steel and Type 304 stainless steel in both real and simulated white water show the effects of pH, temperature and chloride content. Preliminary results for localized corrosion of Types 304 and 316L stainless steel as a function of sulfate to chloride concentration in simulated white water are reported. Corrosion severity increases at sulfate to chloride ratios of 3:1 and less. An improvement in corrosion resistance for Type 316L compared to Type 304 stainless steel under crevice test conditions created by pulp deposits is indicated by these initial results.

INTRODUCTION

Corrosion of papermaking equipment by white water can be caused by constituents as small as ions in 1 ppm concentrations to fiber masses covering several square inches (cm^2). The severity of this damaging process is influenced by the degree of white water closure. The corrosion process consists of specific metal-environment couples. It may be either localized, uniform or both. It is not possible to directly relate all environmental changes to the corrosion rate of a given metal, per se. Rather we must first characterize the particular metal-solution system and analyze the effect of changes on the appropriate corrosion process.

For a given category of paper or board product, white water is derived from fiber, papermaking additives and raw water. Substantial quantities of water are carried with the fiber from the pulp source (pulp mill, bleach plant or nonintegrated pulp sources) to the blending chest and refiners. Additional water is introduced after refining and prior to cleaning; in most cases this water originates from the paper machine. Finally water is added with papermaking chemicals, e.g., sizing, and for consistency regulation at the fan pump prior to the headbox. Since both quantity and quality of these component sources of white water can vary with the papermaking operation (e.g., product type, color change, upsets, etc.), the final chemical composition of the water at the paper machine is unique to each individual mill regardless of category and/or paper product.

In general, white water closure affects corrosivity by a substantial increase of dissolved solids, temperature and biological activity. Both organic and inorganic constituents in the dissolved solids influence the severity of corrosion and most significant among these are chlorides, sulfates, lignin-related sulfur compounds, organic acids and carbonates. No data are available which identify quantitative changes in all of these constituents as a result of closure. Temperature will increase with closure and some mills report values as high as 150°F (66°C)[1]. Higher temperatures increase both the activation of localized corrosion and metal dissolution kinetics in uniform attack. Biological activity is retarded with higher temperature but the predominance of nutrients for bacterial growth makes the use of biocides and slimicides mandatory for most closed white water systems. This is particularly true with high capacity systems where there are many stagnant, quiescent locations and/or systems where the frequency of cleanups is low. Bacterial growth in these favorable sites causes severe pitting corrosion of even the highly alloyed specialty stainless steels.

WHITE WATER CORROSION

In the past, reports of white water corrosivity were related to specific corrosion failures in the paper mill. These were reviewed in an earlier paper[2]. More recently, investigators have discussed either the likely forms of corrosion and its control or the choice of construction materials in paper machine design[3,4]. At present, surveys are underway to characterize the properties of various white water systems, define a relative measure of its corrosivity and determine the present status of white water closure within the industry[5,6].

Our research program in white water corrosion is twofold: First, to analyze the effect of dissolved solids buildup on the uniform corrosion of mild steel and Type 304 stainless steel, second, to identify critical operating conditions within the white water environment which accelerate localized corrosion (pitting, crevice attack) at "deposits" on stainless steel surfaces. A necessary follow-up to these studies includes the appropriate corrosion control measures applicable to papermaking hardware which operates in "closed" white water systems.

EVALUATION OF UNIFORM CORROSION

The initial steps in our current program to evaluate papermaking environments consisted of simple experiments which relate the uniform corrosion behavior of mild steel as a function of environmental pH, electrical conductivity, and chloride content.

Polarization tests were conducted in distilled water adjusted to various pH and chloride levels by addition of sodium hydroxide, sodium chloride and sulfuric acid. The pH range varied from below neutral (pH 6.0) to highly alkaline (pH 13) while chloride content at each pH varied from 200 to 4000 ppm. Electrical conductivity was also measured for each solution.

The polarization behavior indicated that diffusion controlled cathodic kinetics control the uniform corrosion rate of mild steel in waters of pH 6.0 to approximately 11.0, regardless of chloride content. The effect of higher chloride concentration is to increase the diffusion limiting current density and thus the

corrosion rate. Figure 1 shows this behavior which was obtained at pH 7 and it is representative of that found in waters adjusted to the pH 6-11 range. Note the increase in limiting cathodic current density with increase in chloride content.

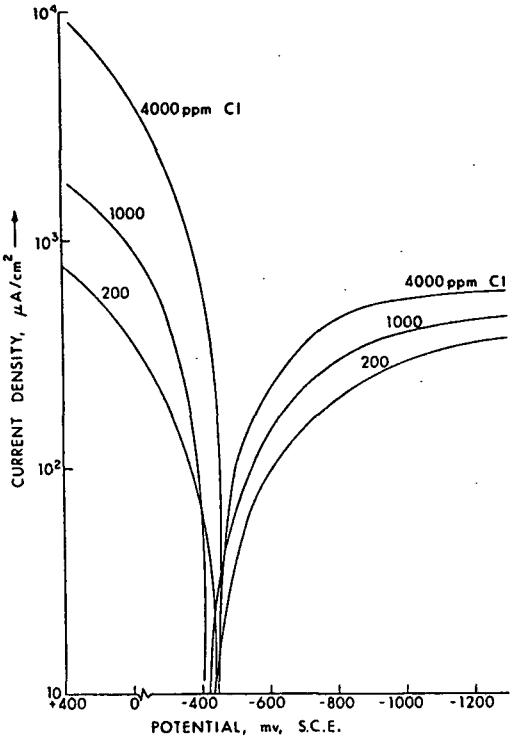

Figure 1. Polarization Behavior of Mild Steel in pH 7 Water with 200, 1000 and 4000 ppm Chloride.

In the range of approximately pH 11, the polarization behavior changes to that commonly observed for active-passive systems. Again, this occurs regardless of chloride content. In these systems the uniform corrosion rate is determined by the passive current density which represents a relatively low corrosion rate. Figure 2 shows this behavior at pH 13. In this case the effect of increased chloride is to increase corrosion in the passive state but the magnitude of this increase is seen to be very small.

Therefore, the overall evaluation of mild steel corrosion in water as a function of pH and chloride is determined by its change from an active to active-passive behavior. Figure 3 shows that the increase in corrosion due to increased chloride is most significant when the metal is corroding in an active state (pH 6 to approximately 10) as compared to that for passive behavior (pH 11-13).

The relationship of solution electrical conductivity to corrosion rate was found to be similar. Figure 4 shows that the corrosion rate of mild steel is only related to the electrical conductivity of the solution in the lower pH range. This seems to indicate that in the case of mild steel corroding actively in waters made more aggressive by high chloride content, the trend of increased conductivity correlates with increased corrosion rate. However, iron corroding in the passive state shows little, if any, change in dissolution rate with changes in solution conductivity. Preliminary tests of mild steel in mill white water confirm this trend as shown by the indicated points (Fig. 4).

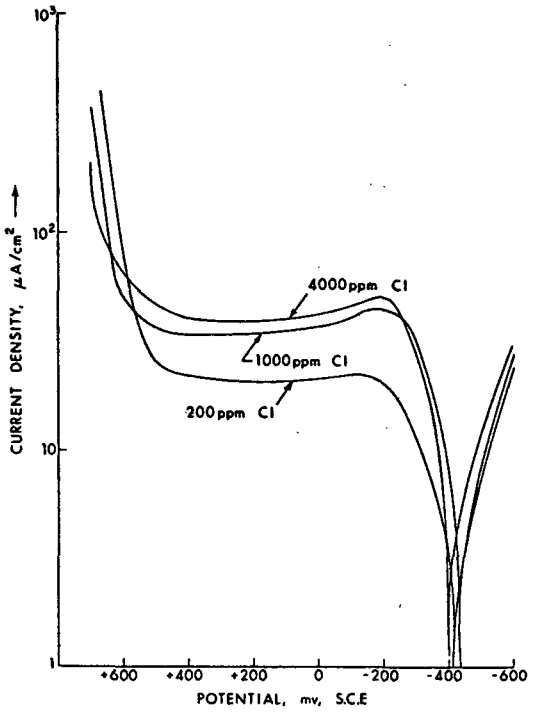

Figure 2. Polarization Behavior of Mild Steel in pH 13 Water Containing 200, 1000 and 4000 ppm Chloride.

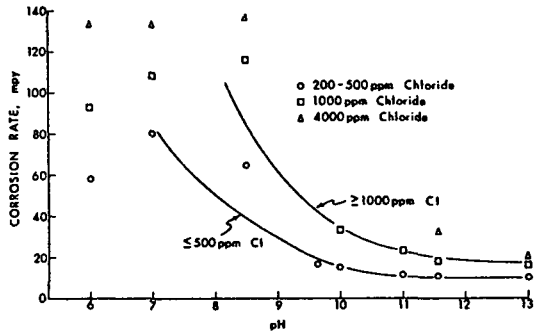

Figure 3. Corrosion Rate of Mild Steel in Water as a Function of pH and Chloride Content.

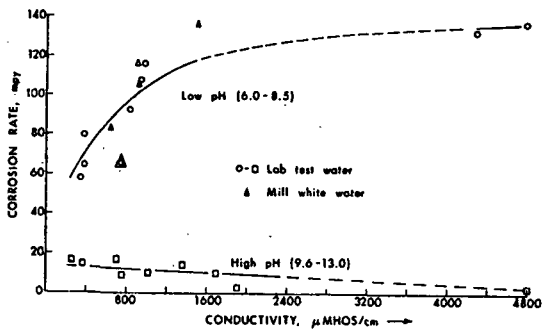

Figure 4. Corrosion Rate of Mild Steel in Water as a Function of the Solution's Electrical Conductivity and pH.

The electrical potential which exists on a metal freely corroding in its environment (called the corrosion potential) can be observed to change with time either by altering environmental properties or surface characteristics of the metal itself. For example, the relative stability of protective surface films can be

determined by potential decay measurements[7]. We then looked at the corrosion response of mild steel and Type 304 stainless steel to both simulated and real white water systems by using these techniques.

The simulated white water consisted of distilled water containing 5, 10, 20 and 50 thousand ppm dissolved solids. The concentration of each constituent in the dissolved solids (shown in Table I) was based on the reported compositions given previously[2] but the level of chloride was intentionally increased to simulate chloride build-up in future closed systems. The pH was adjusted to 5.0 by alum/sulfuric acid additions and measurements were made in room temperature, stirred and aerated solutions.

TABLE I

CONSTITUENT CONCENTRATION IN MAKE-UP OF SIMULATED WHITE WATER ENVIRONMENTS

Constituent	Added, %	Additive Used
Sulfate	40.0	Sodium sulfate plus others as shown below
Chloride	10.0	Sodium chloride
Sodium	45.0	All sodium compounds shown
Aluminum	1.0	Alum
Calcium	0.5	Calcium sulfate
Potassium	1.0	Potassium sulfate
Silicon	1.5	Sodium silicate
Magnesium	1.0	Magnesium sulfate

Figure 5 shows the potential decay behavior for the referenced metals in simulated white water environments. The results for Type 304 stainless steel indicate film growth and stability after a few hours regardless of dissolved solids content. Mild steel shows a similar behavior at levels of dissolved solids greater than 5000 ppm. In solutions of lower dissolved solids content, a continuous film breakdown occurs, indicative of an actively corroding metal undergoing uniform or general attack. The initial results from field tests in white water of a low dissolved solids level, i.e., small degree of closure, seem to confirm this pattern as shown by the indicated points in Fig. 5.

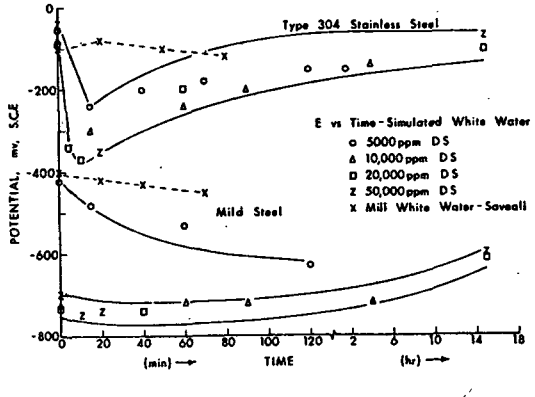

Figure 5. Potential Decay Curves for Mild Steel and Type 304 Stainless Steel in Simulated and Real White Water Environments.

The polarization behavior of mild steel in these simulated white waters was very similar to that described for lab test waters in the lower pH range, namely, rate limited, diffusion controlled cathodic kinetics. As predicted by the potential decay results, the magnitude of corrosion (cathodic) kinetics was substantially reduced in water containing dissolved solids higher than 10,000 ppm. The electrode surface was uniformly coated with a film build-up, which results in much lower corrosion rates (Table II).

TABLE II

CORROSION BEHAVIOR OF MILD STEEL AND TYPE 304 STAINLESS STEEL IN SIMULATED WHITE WATER

Simulated White Water (ppm Dissolved Solids)	Polarization Behavior		Corrosion Rate (mpy) av.		Galvanic Current Density Type 304 to Mild Steel ($\mu A/cm^2$)
	Type 304	Mild Steel	Type 304	Mild Steel	
5,000	Passive	Active (diffusion controlled cathodic kinetics)	1.37	106	155
10,000	Passive	Active (diffusion controlled cathodic kinetics)	2.16	126	59
20,000	Passive	Active (diffusion controlled cathodic kinetics)	1.10	55.6	46
50,000	Passive	Active (diffusion controlled cathodic kinetics)	1.20	41.1	52

The measurements of galvanic current density (also shown in Table II) between mild steel and Type 304 stainless steel also demonstrated this effect of increased dissolved solids. In this case, passage of galvanic currents were impeded by film build-up shielding cathode reduction sites and opposing the increased conductivity at higher concentration of dissolved solids.

Field test results of the same metals exposed to white water in semiclosed systems demonstrate behavior similar to that found in the simulated environments of low dissolved solids content. Table III shows the results obtained at various paper machine locations. The effect of lower pH and/or higher temperature is reflected by the higher corrosion rates measured at wire tray, saveall and vacuum pump locations.

TABLE III

FIELD TEST RESULTS FOR CORROSION RATE OF MILD STEEL AND TYPE 304 STAINLESS STEEL IN PAPER MACHINE WHITE WATER

Paper Machine Location (producing fine paper)[a]	White Water		Corrosion Rate (mpy)	
	pH	Temperature, °F	Mild Steel	Type 304
Wire pit	7.4-7.8	72	27.8-37.4	0.13
Wire tray	4.5-6.7	72-80	65.0-68.0	0.24-0.33
Wire tray	4.5-6.7	95-120	116.0	0.60-0.76
Wet lap	7.8	86	50.5	0.21
Saveall discharge	6.0	86	176.9	1.20
Saveall return	6.1	86	197.1	0.46
Vacuum pump discharge	6.6	105	65.7	0.23

[a] Semiclosed operation: 35-50% closed system.

EVALUATION OF LOCALIZED CORROSION

Most wet end paper machine components are constructed of stainless steel. The grades most common in paper machines today are Types 304 and 316L stainless steel. A major corrosion problem is one of localized attack beneath fibrous deposits formed by stock hang-ups and scale forming elements in the pulp/white water environment. In particular, severe pitting and/or crevice corrosion conditions exist in fibrous deposits on many stainless steel components, e.g., headbox, slice lip, foil support boxes, suction rolls, etc.

Our research program is now aimed toward a better definition of "deposit" corrosion as influenced by the interaction of species known to be present in white water/fiber deposit crevices, e.g., chemical components (sulfate, chloride, etc.), dissolved gases, bacteria, etc. This study seeks to establish the interaction of the critical white water properties (chemistry) and

papermaking operating conditions (temperature, fiber type, pH, biological activity, etc.) which activate the "deposit" corrosion cells as influenced by white water closure.

Since the program is just underway, only preliminary results of the first phase of the study can be reported at this time. The object of initial testing was to study the influence of sulfate and chloride concentrations in white water on the corrosion behavior of Types 304 and 316L stainless steel. Simulated white water solutions which were treated with alum/sulfuric acid to pH 5.0 were prepared at a total dissolved solids concentration of 5000 ppm (mg/l). Table IV shows the solution formulation and the six sulfate to chloride concentrations for these tests.

TABLE IV

FORMULATION OF SIMULATED WHITE WATER

[pH 5.0, 5000 ppm (mg/l), Total Dissolved Solids, 115°F]

Fixed Ionic Concentration

Type	Amount, %	Additive
Ca	0.5	Calcium sulfate
Mg	1.0	Magnesium sulfate
K	1.0	Potassium sulfate
Si	1.5	Sodium silicate
HCO_3	2.0	Sodium bicarbonate
Al	1.0	Aluminum sulfate

Variable Ionic Concentration

Solution	Sulfate, %	Chloride, %	Sulfate:Chloride Ratio	Solution Conductivity (μMHOS/cm)
1	30	3	10:1	3252.8
2	30	6	5:1	3445.1
3	30	10	3:1	3849.8
4	30	15	2:1	4378.4
5	30	30	1:1	7222.4
6	20	40	1/2:1	7961.3

Base line experiments consisted of polarization and potential decay tests on bare (uncreviced) specimens of Type 304 and 316L stainless steel. The polarization behavior of Type 304 in each solution is shown in Fig. 6. As expected, the tendency for pitting corrosion increases significantly at lower sulfate:chloride ratios. This is most apparent at ratios of 3:1 or less. Potential decay measurements on Type 304 (Fig. 7) indicate a consistent trend toward more noble potentials regardless of sulfate:chloride ratio. This means that Type 304 will be in a passive condition upon immersion in these white water solutions but with longer exposure times there is a strong tendency toward pitting, particularly with chloride buildup of 1500 ppm (mg/l) or higher, i.e., sulfate:chloride ratios of 1:1 and less. These same tests are in progress on Type 316L stainless steel.

Crevice corrosion beneath fiber deposits is under study on the same materials. A Teflon specimen holder with a circular window exposing 15.5 cm^2 of a stainless steel plate is used to test different fiber-white water combinations. The fiber deposit is a 1 cm^2 circular piece cut from a handsheet of known fiber type and measured caliper. This arrangement is shown in Fig. 8. The deposit is held against the stainless steel surface by a clamp at fixed pressure. Electrical hook-up wiring inside the Teflon holder allows electrochemical measurements of the plate-fiber system. A photograph of this system immersed in white water is shown in Fig. 9. The initial tests were conducted to determine the activation of deposit corrosion as a function of white water composition. Simulated white water of different sulfate-chloride contents, described above, were used in these tests. Corrosion current density was measured as a function of applied anodic potential in solutions 1-5, Table IV. The point of crevice cell activation was taken as that applied potential where the anodic current increased continuously. The plate was removed at that point, examined microscopically, and found to be severely corroded in the crevice area.

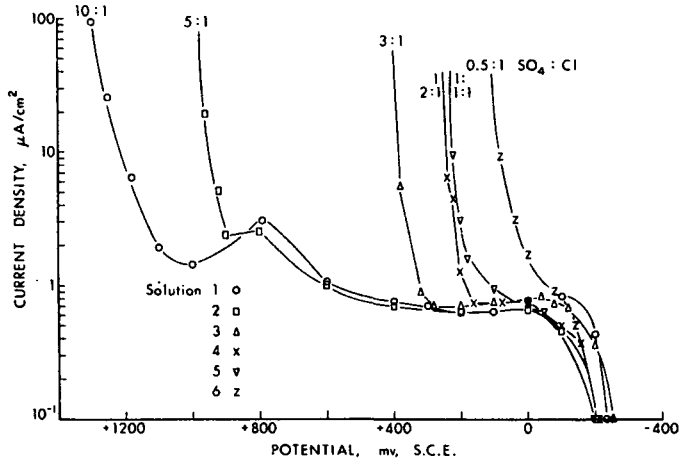

Figure 6. Anodic Polarization Behavior Type 304 Stainless Steel in Simulated White Water.

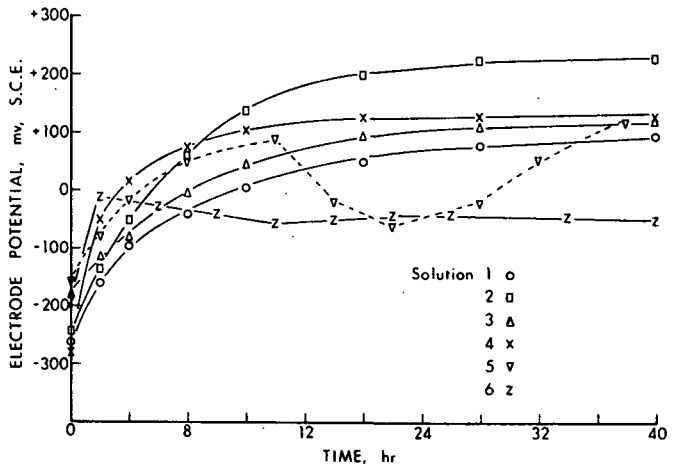

Figure 7. Potential Decay Behavior Type 304 Stainless Steel in Simulated White Water.

The results of these determinations for both Type 304 and 316L and unbleached, kraft, softwood deposits in five white waters of different sulfate to chloride ratios is shown in Table V. The data show the open circuit potential (freely corroding state, 25 minutes after immersion) and the breakdown or activation potential for "deposit" corrosion. The difference between these values provides a relative measure of the margin of safety for deposit corrosion as a function of sulfate to chloride concentrations in the simulated white water. Using the same measure for pitting corrosion, based on polarization test results, the margin of safety for localized corrosion is shown in Table VI. The larger values correspond to a greater margin of safety.

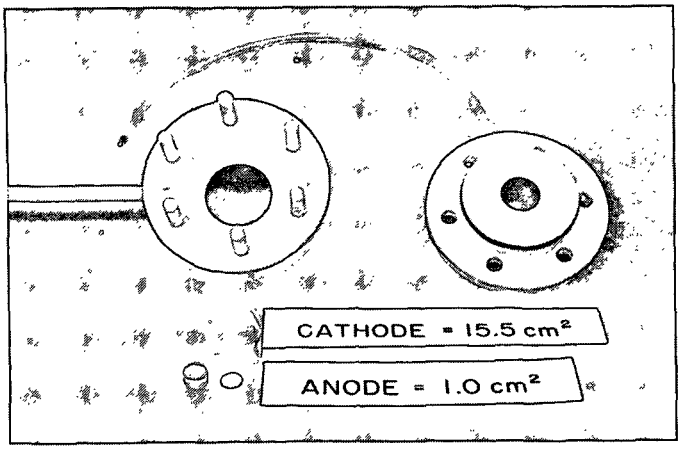

Figure 8. Photograph of Teflon Specimen Holder, Stainless Steel Plate and Fiber Deposit for Localized Corrosion Study.

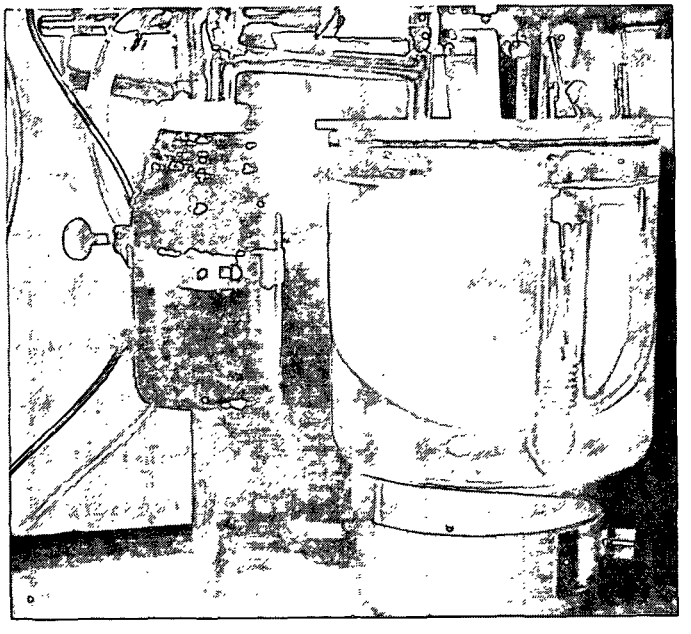

Figure 9. Photograph of Specimen Apparatus, in situ.

TABLE V

DEPOSIT CORROSION DATA FOR TYPES 304 AND 316L STAINLESS STEEL IN SIMULATED WHITE WATER[a]

Solution No.	SO_4:Cl Ratio	Electrochemical Potentials (mv, S.C.E.) Type 304 Open Circuit	Type 304 Activation Potential	Type 316L Open Circuit	Type 316L Activation Potential
1	10:1	-215	+700	-213	>1000
2	5:1	-230	+300	-227	+460
3	3:1	-250	+300	-250	+340
4	2:1	-197	+260	-252	+320
5	1:1	-170	+75	-243	+150
6	1/2:1	-260	+20	-248	+90

[a]Simulated white water compositions are given in Table IV.

TABLE VI

SUSCEPTIBILITY OF TYPES 304 AND 316L STAINLESS STEEL TO LOCALIZED CORROSION IN WHITE WATER[a]

Solution No.	SO_4:Cl Ratio	Margin of Safety (mv) Pitting Corrosion Type 304	Pitting Corrosion Type 316L	Deposit Corrosion Type 304	Deposit Corrosion Type 316L
1	10:1	1330	>1250	915	>1213
2	5:1	1110	1250	530	687
3	3:1	579	1064	550	590
4	2:1	431	958	457	572
5	1:1	358	468	245	393
6	1/2:1	240	400	280	338

[a]White water composition in Table IV.

The results indicate an increased tendency for pitting and crevice corrosion attack in waters containing sulfate to chloride ratios of 3:1 or lower. There is an indication of an improved margin of safety for pitting in Type 316L over Type 304 stainless steel in the crevice-free state. There also appears to be some advantage in the corrosion resistance of Type 316L to deposit attack but these observations require further testing.

We are only in the initial stages of this investigation and plan to study a number of white water properties — compositions, pH, temperature dissolved gases and biological activity. The choice of these environmental variables for different fiber deposits will become much more selective as we receive more input from the paper industry regarding their white water systems, via survey and direct mill contact[5,6]. Our plans also include an appraisal of suitable corrosion control measures, e.g., white water treatments, more resistant materials, coatings, inhibitors, etc.

GENERAL OBSERVATIONS

It is too early in our program to ascribe definite conclusions regarding the corrosivity of white water in closed systems. Based on the preliminary investigation described above, the following trends can be enumerated.

1. The corrosion rate of mild steel in near neutral pH water is limited by diffusion controlled cathodic kinetics which increase with higher concentration of chloride.
2. Mild steel actively corroding in near neutral pH water containing chloride transforms to active-passive behavior at higher pH and a reduced corrosion rate. The assessment of reduced corrosion rate in high pH water refers to uniform or general corrosion and not to pitting attack.
3. Electrical conductivity of the solution appears to correlate better with corrosion of mild steel in the active state rather than that for the passive condition.
4. Potential decay measurements indicate a change in protective film stability for mild steel in waters which contain above 5000 ppm dissolved solids. This change results in lower uniform corrosion rate for both mild steel and Type 304 stainless steel, particularly above the 10,000 ppm dissolved solids level. This suggests that studies of pitting and/or crevice corrosion may be more significant in waters containing high contents of dissolved solids.
5. Studies of localized corrosion on Types 304 and 316L stainless steel show the effect of sulfate to chloride concentrations in simulated white water containing 5000 ppm (mg/l) total dissolved solids.

A greater tendency toward pitting and "deposit" corrosion attack is observed at sulfate to chloride ratios of 3:1 and less.

6. Type 316L stainless steel demonstrated improved resistence to the activation of localized corrosion in all solutions regardless of sulfate to chloride ratios.

EXPERIMENTAL

Electrochemical tests were used to determine corrosion rate, corrosion potential decay, galvanic compatibility (mild steel to Type 304), and complete polarization behavior of these metals in each environment. The test equipment consisted of a potentiodyne analyzer[a], commercial grades of mild steel, Type 316L, and Type 304 stainless steel as working electrode, Lazaran (silver-silver chloride) or calomel (mercury-mercury chloride) reference electrodes and platinum or similar material as counterelectrodes. Lab test environments for uniform corrosion were at room temperature, well aerated and stirred, while field test condition depended on machine location. Localized corrosion tests in simulated white water containing different sulfate-chloride concentrations were conducted at 115°F (46°C).

[a]Trade name — Petrolite Instruments, Petreco Division, Petrolite Corporation.

ACKNOWLEDGMENTS

The author expresses his special thanks to Thilmany Pulp and Paper Company and Fox River Paper Company for their assistance in this study.

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